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Report No. 6

RESEARCH ON ELECTROCHEMICAL ENERGY CONVERSION SYSTEMS

Interim Technical Report

By

R. T. FDLEY, D. H. BDMKAMP,

and W. R. BAIRD

February 1969

To

U. S. ARMY MOBILITY

EQUIPMENT RESEARCH AND DEVELOPMENT CENTER

Fort Belvoir, Virginia

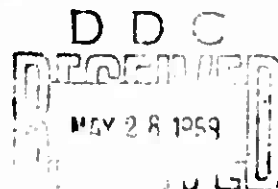
Prepared By

The American University

Washington, D. C.

Contract No. DA-44-009-AMC-1386(T)

DA Project/Task Area/Work Unit No. 1T061102A34A 00 023 EF



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STATEMENT #2 UNCLASSIFIED February 1969

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SUMMARY

The investigation of electrochemical energy conversion systems has involved two specific tasks. The first has dealt with measurements of the solubility of oxygen in organic liquids which might provide the basis for high energy batteries. The solubility of oxygen in γ -butyrolactone is 5.5 ml/100 ml, in propylene carbonate, 1.7, in dimethyl sulfoxide, 3.7, and in N-nitrosodimethylamine, 6.6. The physical method used for these determinations gives results about 2.7% low when compared with literature values for the solubility of oxygen in water. No change in solubility was observed in butyrolactone due to the presence of added electrolyte - up to 0.8 M lithium perchlorate.

The second task deals with the mathematical analysis of electrochemical energy conversion devices. Attention was given to the solution of kinetic equations describing the hydrogen-deuterium exchange of an hydrocarbon on a catalytic surface saturated with deuterium. Kinetic expressions for a five step successive reaction for methane are solved by matrix techniques. These techniques should be conveniently handled by a digital computer and the expressions can be corrected for temperature, flow rates, and other experimental parameters.

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series of solvents. This plot is usually linear and shows a linear relationship between $\log i$, $\log \gamma$ and γ (3). This relationship has been expressed by Eq. (4) as:

$$\log i = - \frac{4\pi r^2 \sigma}{2.303 RT}$$

or, the energy required to form a cavity in a liquid surface is proportional to the product of the surface tension and the area of the cavity. This expression holds for simple and convenient solvent systems but fails for more complex systems.

The solubility has also been correlated as a function of solvent internal pressure (dP/dT), with the higher internal pressures being associated with the lower gas solubility (5).

From an empirical standpoint it has been observed that the solubility of a gas will increase as a function of its molecular weight and size. For simple mono- and diatomic gases the order is N_2 , H_2 , CH_4 , O_2 , and Ar .

C. Methods for Determining Solubility of Gases in Liquids.

Many methods are reported in the literature and generally they may be placed in one of the following three categories:

- a) analytical
- b) electrochemical
- c) physical.

The most common method for the determination of K_H is in a liquid in the form of a gas (6). This is the case with the determination of oxygen in water and a number of other gases. However, for the effecting side reaction, the solubility of oxygen in

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1. Introduction

This is the sixth semi-annual report of research on high-energy electrochemical energy conversion systems. Up until now the overall program has been divided into seven tasks:

1. Determination of open circuit potentials of a series of couples in various electrolytes, and at appropriate temperatures;
2. Determination of the reversibility of these couples;
3. Electrochemical studies of high-energy couples leading to evaluation of these couples as materials for construction of high-energy, electrically rechargeable storage systems;
4. Determination of kinetic parameters and evaluation of the rate limiting factors of selected reactions of electrochemical couples at appropriate electrodes;
5. Determination of kinetic parameters of selected reactions at catalytic electrodes;
6. Investigation of ion transport processes in membranes and/or electrolytes at elevated temperatures, and
7. A detailed analysis of performance characteristics of electrochemical energy conversion devices.

The first five semi-annual progress reports described work on Tasks 1, 2, 3, 4, 5, and 7. During this reporting period work continued on Tasks 4 and 7.

II. TASK FOUR - OXYGEN ELECTRODE IN PROPYLENE CARBONATE

A. Objective

In the third progress report (1) on this project the concept and theoretical advantages of the air electrode were discussed. To interpret the experimental results from mass transport considerations it is necessary to know the solubility of O_2 in propylene carbonate. To correlate our results with those obtained in other systems it is required to know the solubility of oxygen in organic solvents such as γ -butyrolactone, dimethyl sulfoxide, dimethyl formamide, and N-nitrosodimethylamine. A survey of the literature failed to yield the pertinent data on the solubility of O_2 in these solvents. For these reasons the solubility of O_2 was measured in a number of organic solvents.

B. Solubility of Gases in Liquids

There have been many approaches to the explanation of gas solubility in liquids including various ways of treating the experimental data. Some of these are discussed in the monograph by Hildebrand and Scott (2). None of the approaches have been universally applicable.

One of the more successful treatments of solubility data utilizes a plot of $\log L$ (Ostwald absorption coefficient*) against σ (solvent surface tension) for a given gas in a

* $L = v_g/V_s$ where v_g is volume of gas absorbed and V_s is volume of solvent absorbing.

series of solvents. This plot is usually linear and shows the relationship between $\log L$ and r (3). This relationship has been represented by eqn. (4) as:

$$\log L = - \frac{4 \pi r^2 \sigma}{2.303 RT} + C$$

or, the energy required to form a cavity in a liquid surface is proportional to the product of the surface tension and the area of the cavity. This expression holds for simple and convenient solvent systems but fails for more complex systems.

The solubility has also been correlated as a function of solvent internal pressure (dP/dT), with the higher internal pressures being associated with the lower gas solubility (5).

From an empirical standpoint it has been observed that the solubility of a gas will increase as a function of its molecular weight and size. For simple non- and diatomic gases the order is N_2 , H_2 , O_2 , CO , and CH_4 .

C. Methods for Determining Solubility of Gases in Liquids.

Many methods are reported in the literature and generally they may be placed in one of the following three categories:

- a) analytical
- b) electrochemical
- c) physical.

The most common analytical method for the determination of C_g is in a liquid is the ebullition method. With this method the gas is bubbled through a liquid and the gas is collected in a graduated gasometer or a similar device. The volume of gas collected is measured and the solubility is determined from the ideal gas law.

fication of the apparatus used by Harrison and Millett (9). This method was found sufficient to furnish results of the desired accuracy, i.e. about 1%. The apparatus was constructed relatively easily using commercially available glassware. It was possible to connect the apparatus to the existing vacuum distillation system so that an organic liquid could be degassed by vacuum distillation and the receiver for the distillate could become the reservoir for the gas solubility apparatus. Other modifications to the apparatus were possible to yield greater accuracy but the increased expense and difficulty of operation could not be justified.

The apparatus is schematically shown in figure 1 and is pictured along with the vacuum distillation apparatus in figure 2. This apparatus consists of two calibrated gas burettes joined at their bottoms. One of the burettes is attached to a rough liquid manometer to allow for maintenance of atmospheric pressure in one-half of the system. A large glass spiral is mounted on top of the other burette and provides a large area for gas absorption. As the degassed liquid is dripped from the reservoir into the spiral the liquid will flow down through the spiral as a thin film.

A maximum surface area for absorption will then be presented to the gas. The space in the two burettes is separated by a U-shaped column of liquid so that there is a decrease of pressure in the absorption burette while in the spiral, until atmospheric pressure is maintained in the reservoir. The amount of gas absorbed is equal to the volume difference between the two burettes for the major pressure of the solvent.

The experimental procedure is carried out as follows:

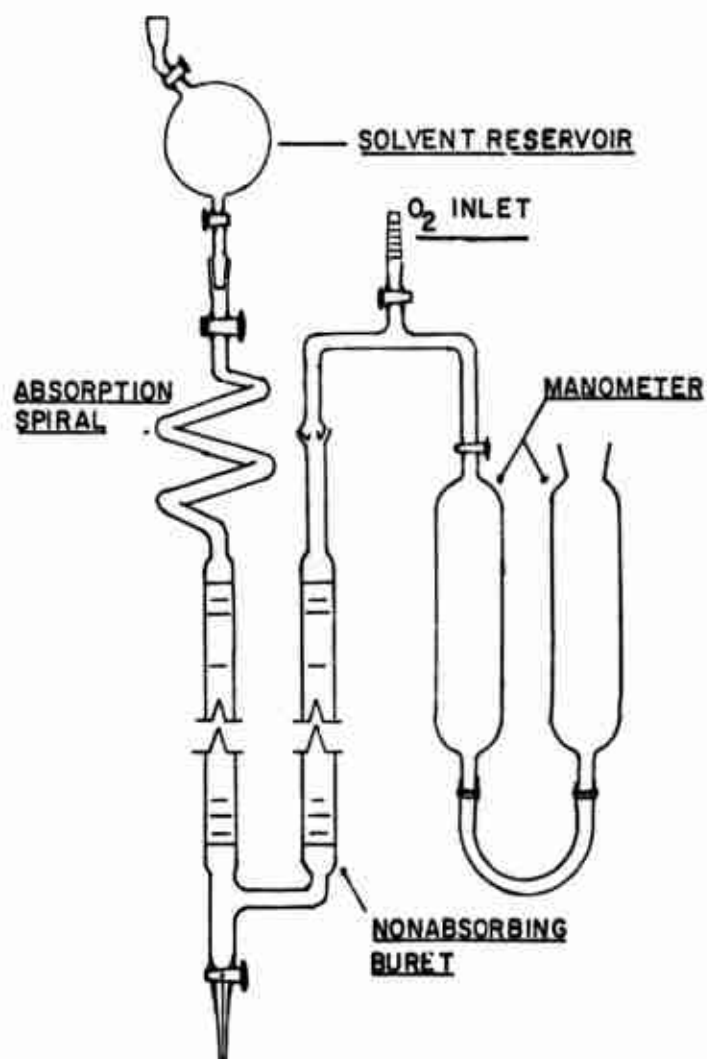


Figure 1. Apparatus for the measurement of the rate of absorption of oxygen into a liquid.

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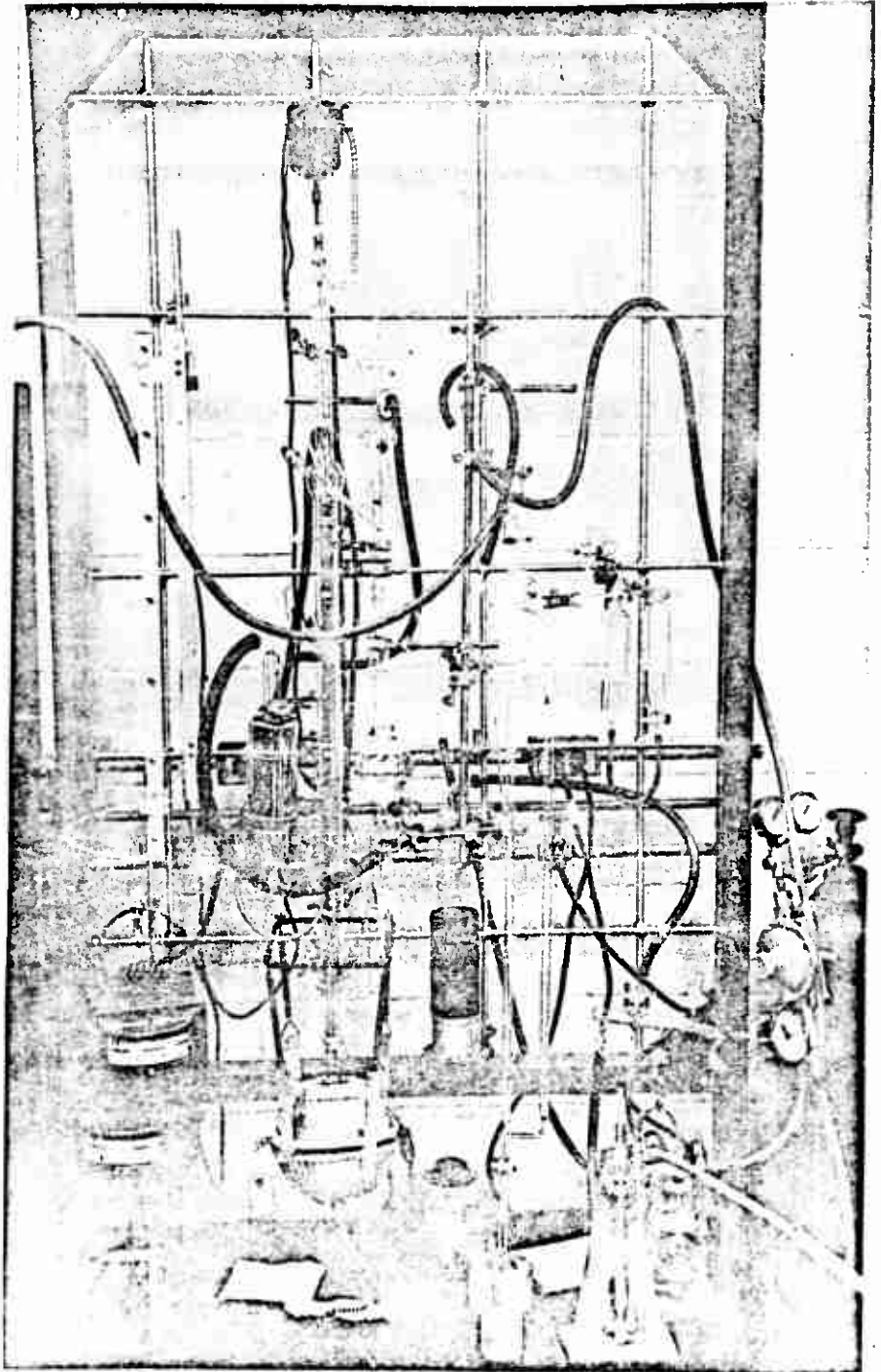


Figure 2. Gas solubility apparatus and vacuum distillation equipment.

1) The solvent is degassed. This is accomplished by vacuum distillation using the Nestor-Faust spinning band distillation column. The distillate is collected in a flask which is then attached to the top of the absorption apparatus via a ground glass fitting.

2) The U-portion connecting the two burettes is filled with pure solvent until the liquid stands at the zero level in both burettes.

3) The oxygen gas is flowed through the two burettes to completely fill them and to saturate the U- portion of solvent.

4) Both columns of gas are returned to atmospheric pressure and all outlets to the atmosphere are closed off.

5) The solvent in the reservoir is slightly pressurized with hydrogen to assure that it will flow into the apparatus. This is done through a gas inlet tube connected to the sample reservoir flask.

6) The solvent is dripped into the absorption spiral at a rate of about 2.5 ml/minute and collected in a volumetric flask as it flows out of the burette at the same rate.

7) After collecting some appropriate volume in the volumetric flask, such as 100 ml, the burettes are drained until the non-absorption side reads 0.0 ml. This indicates that that side is at atmospheric pressure. The amount of solvent above 0.0 in the absorption side is the amount of O_2 absorbed; this must be added to the volume collected.

E. Results and Discussion

One important modification made in the apparatus over that described by Morrison and Billett (9) involved the use of a slight pressure head to maintain a flow of solvent into absorbing burette. This pressurizing gas will be absorbed to some degree and then will be released into the spiral. This obviously decreases the observed solubility of oxygen in the organic

liquid by some magnitude. If the pressurizing gas is oxygen a large negative error would be expected. If the pressurizing gas were N_2 , or H_2 a smaller error would be expected and the question was whether the error would be small enough to be tolerated. To investigate this effect and also to study the precision and accuracy of the method, a number of experiments were performed with water as the solvent. These values are reported in Table I. As expected, when O_2 was used as the pressurizing gas the values were quite low--by 58%. Although the pressurizing gas does not saturate the water during the time of exposure in the reservoir, considerable gas is absorbed. A series of experiments with N_2 as the pressurizing gas gave results that were 7.1% too low while H_2 produced an error of - 2.1%. The nitrogen runs are not replicates as certain improvements in technique were introduced as the experimental work progressed. For example, in the early work the elapsed time between degassing the solvent and running the experiment was often several hours. Values closer to the accepted literature value were obtained when the experiment was performed directly after degassing through vacuum distillation. Experiments N3, H1, and H2 were run in this manner and the average coefficient, 0.0277, was lower than the accepted 0.02847 value (8) by 2.7%. The results given below for oxygen solubilities in the organic liquids should then be assumed to be low by about 3% assuming that the solubility behavior in these organic solvents is similar to that in H_2O .

In Table II are given solubilities of oxygen in γ -butyrolactone, propylene carbonate, dimethyl sulfoxide, and N-nitrosodimethylamine.

Table 1. Solubility of O_2 in water ($25 \pm 0.5^\circ C$)

$T, ^\circ C$	Pressurizing Gas	O_2 absorbed (ml/100 ml.)	O_2 absorbed (ml/100 ml.)	Atmospheric pressure (mm. Hg)	C_{O_2}
21	O_2	3.1/101.3	3.0	761	0.0273
22	O_2	3.1/101.3	3.0	751	0.0271
21	O_2	5.4/295	3.05	-	0.0268
22	O_2	10.5/350.9	2.7	-	0.0254
23	O_2	3.0/105	2.9	-	0.0274
24	O_2	7.0/252.8	2.4	-	(0.0237)
01	O_2	2/101	1.1	754	0.0175
01	O_2	1.2/101	1.0	754	0.0170
03	O_2	1.4/100	0.67	752	0.0063
01	O_2	1.1/100	1.1	761	0.0104
05	O_2	1.7/101	0.95	763	0.00903

Atmospheric pressure

0.0285

* Calculated from $C_{O_2} = \frac{P_{O_2} \cdot V_{O_2}}{V \cdot 760}$ where V_{O_2} is the volume of O_2 absorbed

and V is the volume of water

Table II. Solubility of Oxygen in Organic

Solvents ($25 \pm 0.5^\circ\text{C}$)

Solvent	Solubility (ml/100 ml)	Average s	Lit. nature Value
n-butyrolactone	5.2	0.0499	
	5.6		
	5.8		
	5.2		
Propylene carbonate	1.7	0.0153	
	1.6		
	1.7		
	1.7		
Dimethyl sulfoxide	3.8	0.0382	0.015 g ₂ /100g (10)
	3.8		
	3.7		(0.04 g ₂ /100 g ₂)
	3.6		
N-nitrocellulose- amine	6.6	0.0665	5.8 g ₂ /100 g ₂ (11) (11 g ₂ + 0.01/100 ml)
	7.1		
	6.0		

There is not much good data in the literature to cover these results, but the experimental work of K. L. B. Smith and J. H. D. Ewart (1936) is the most extensive. They found that the solubility of $\text{C}_6\text{H}_5\text{NO}_2$ in various solvents is very low, and that the solubility of $\text{C}_6\text{H}_5\text{NO}_2$ in various solvents is very low, and that the solubility of $\text{C}_6\text{H}_5\text{NO}_2$ in various solvents is very low. It would appear that the solubility of $\text{C}_6\text{H}_5\text{NO}_2$ in various solvents is very low, and that the solubility of $\text{C}_6\text{H}_5\text{NO}_2$ in various solvents is very low.

The following table shows the solubility of $\text{C}_6\text{H}_5\text{NO}_2$ in various solvents. The solubility of $\text{C}_6\text{H}_5\text{NO}_2$ in various solvents is very low, and that the solubility of $\text{C}_6\text{H}_5\text{NO}_2$ in various solvents is very low. The solubility of $\text{C}_6\text{H}_5\text{NO}_2$ in various solvents is very low, and that the solubility of $\text{C}_6\text{H}_5\text{NO}_2$ in various solvents is very low. The solubility of $\text{C}_6\text{H}_5\text{NO}_2$ in various solvents is very low, and that the solubility of $\text{C}_6\text{H}_5\text{NO}_2$ in various solvents is very low.

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Table III. Solubility of oxygen in Lithium
Perchlorate - γ -butyrolactone Solutions

Concentration (LiClO_4 %)	Solubility (ml/100 ml)	α
0.2	5.6	0.0513
0.45	5.8	0.0531
0.6	5.4	0.0495
0.8	5.6	0.0513

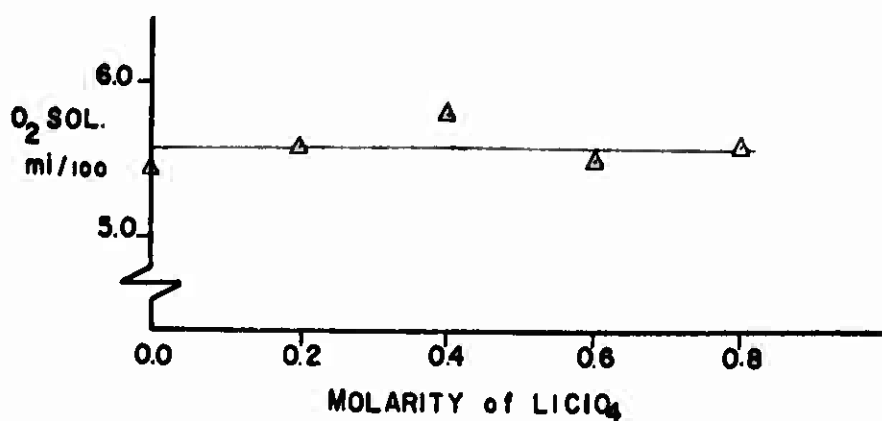


Fig. 3 O_2 SOLUBILITY IN BUTYROLACTONE
vs.
 LiClO_4 CONCENTRATION

a solvent that has saturated with oxygen by mechanical stirring or agitation with a gas diffuser could lead to yield high values. This might account for some of the results reported in the literature that appear to be high.

III. THEORY OF THE KINETICS OF DEUTERIUM- EXCHANGE ON A FUEL CELL CATALYST

A. Background

The reaction of hydrocarbons on a fuel cell catalyst is being studied by observing the H-D exchange of the hydrocarbon on the surface saturated with D₂. Studying the kinetics of this exchange is complicated by the large number of ways in which deuterated species can be formed, which makes solution of the rate expressions difficult. In this section techniques for solving the rate expressions for the successive deuteration of methane are described. Kinetic expressions for first order successive reactions of the type



have been solved for three step irreversible reactions. The rate expressions for the three step successive reaction are:

$$\begin{aligned} \frac{d[A]}{dt} &= -k_1[A] \\ \frac{d[B]}{dt} &= k_1[A] - k_2[B] \\ \frac{d[C]}{dt} &= k_2[B] \end{aligned}$$

These expressions can be integrated to the form:

$$\begin{aligned} [A] &= [A]_0 e^{-k_1 t} \\ [B] &= [A]_0 \left(\frac{k_1}{k_2 - k_1} \right) (e^{-k_1 t} - e^{-k_2 t}) \\ [C] &= [A]_0 \left(\frac{k_1 k_2}{k_2 - k_1} \right) (e^{-k_1 t} - e^{-k_2 t}) \end{aligned}$$

For a five step successive reaction,

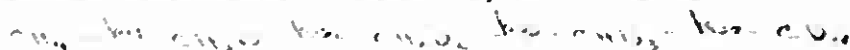


solution of the rate expressions by calculus methods would be difficult.

by use of other techniques, these expressions can be solved more efficiently.

B. Discussion

Solution of the rate expressions for a five step successive reaction would be desirable in order to create a model for reactions such as the successive one site exchange of D for H in CH_4 . When gaseous CH_4 is passed over a catalytic surface which has been exposed to D_2 such that all available sites are assumed to be occupied and only one exchange of D for H is made with each contact of the molecule with the surface, the reaction is:



If it is assumed that the rate of increase of a deuterated species is proportional only to the number of molecules of the lower deuterated species and the probability of transition from one species to the next higher deuterated species, first order reaction kinetics can be used for each transition between species and the rate expressions are:

$$(1) \quad \begin{aligned} \frac{d[\text{CH}_4]}{dt} &= -k_1[\text{CH}_4] \\ \frac{d[\text{CH}_3\text{D}]}{dt} &= k_1[\text{CH}_4] - k_2[\text{CH}_3\text{D}] \\ \frac{d[\text{CH}_2\text{D}_2]}{dt} &= k_2[\text{CH}_3\text{D}] - k_3[\text{CH}_2\text{D}_2] \\ \frac{d[\text{CHD}_3]}{dt} &= k_3[\text{CH}_2\text{D}_2] - k_4[\text{CHD}_3] \\ \frac{d[\text{CD}_4]}{dt} &= k_4[\text{CHD}_3] \end{aligned}$$

The solutions for these expressions are given in Appendix A and are:

(2)

$$[\text{CH}_4] = [\text{CH}_4]_0 e^{-k_1 t}$$

$$[\text{CH}_3\text{D}] = [\text{CH}_4]_0 \left(\frac{k_1}{k_2 - k_1} \right) (e^{-k_1 t} - e^{-k_2 t})$$

$$[\text{CH}_2\text{D}_2] = [\text{CH}_4]_0 \left\{ \frac{k_1 k_2}{(k_3 - k_2)(k_2 - k_1)} (e^{-k_1 t} - e^{-k_2 t}) + \frac{k_1}{k_3 - k_2} (e^{-k_2 t} - e^{-k_3 t}) \right\}$$

$$\begin{aligned}
 (CHD)_2 &= (CHD)_0 \left\{ \frac{k_1 k_2 k_3}{(k_1 + k_2)(k_2 + k_3)(k_3 + k_4)} + \frac{k_1 k_2 k_4}{(k_1 + k_2)(k_2 + k_3)(k_3 + k_4)} + \frac{k_1 k_3 k_4}{(k_1 + k_2)(k_2 + k_3)(k_3 + k_4)} + \frac{k_2 k_3 k_4}{(k_1 + k_2)(k_2 + k_3)(k_3 + k_4)} \right\} \\
 (CHD)_2 &= (CHD)_0 \left\{ 1 + \frac{k_1 k_2 k_3}{(k_1 + k_2)(k_2 + k_3)(k_3 + k_4)} + \frac{k_1 k_2 k_4}{(k_1 + k_2)(k_2 + k_3)(k_3 + k_4)} + \frac{k_1 k_3 k_4}{(k_1 + k_2)(k_2 + k_3)(k_3 + k_4)} + \frac{k_2 k_3 k_4}{(k_1 + k_2)(k_2 + k_3)(k_3 + k_4)} \right\}
 \end{aligned}$$

Larson and Hall (12) assumed the expressions (1) to be applicable in the H-D exchange of CH_4 on a deuterated silica-alumina surface. In the absence of the solutions to all the rate expressions, the authors solved the first rate expression for the value of k_{01} and assumed that the rate of exchange per hydrogen atom is $(\frac{1}{4}) k_{01}$, regardless of the molecule reacting, i.e., $k_{12} = \frac{3}{4} k_{01}$, $k_{23} = \frac{1}{2} k_{01}$, $k_{34} = \frac{1}{4} k_{01}$. This assumption implies that the rate of H-D exchange is constant, with a correction made for the number of H's available. This assumption provided k values for the remainder of the rate expressions which were then numerically evaluated from the experimental data. The values calculated by the authors using this technique were consistent with the experimental values.

As a verification of the concentration expressions (2), the concentration of each of the deuterated species was calculated using the author's calculated value of k_{01} and the assumptions $k_{12} = \frac{3}{4} k_{01}$, $k_{23} = \frac{1}{2} k_{01}$, $k_{34} = \frac{1}{4} k_{01}$. The calculated values agree with the experimental values within experimental errors, indicating that the assumptions regarding the k values are reasonable. However, with the concentration expressions (2), it would not have been necessary to make any assumptions regarding the k values, as each k can be solved for independently using these expressions.

Since the probability of a H-D exchange does appear to be independent of the specie reacting, a binomial distribution of the deuterated species when at equilibrium is suggested where $p = 1/4$ and $P_n = \frac{4!}{n!(4-n)!} p^n (1-p)^{4-n}$. The use of the binomial distribution is allowed by inspecting the manner in which each of the deuterated specie is formed. For example, in order to form D_2 , there must have been two contacts of the CH_4 molecule with the surface in which an H-D exchange occurred, and two contacts with the surface in which an H-D exchange did not occur. If $p = 1/4$ is the probability of any particular H of CH_4 exchanging on the surface, then the probability of two successful exchanges and two unsuccessful exchanges is $p^2(1-p)^2 = (1/4)^2(3/4)^2$. Since the number of ways in which four H atoms taken two at a time can be arranged is $\frac{4!}{2!(4-2)!} = 6$, the total probability of forming D_2 is $P_2 = \frac{4!}{2!2!} (1/4)^2 (3/4)^2 = .211$.

The calculated values are:

$$P_0 = .211$$

$$P_1 = .422$$

$$P_2 = .211$$

$$P_3 = .047$$

$$P_4 = .009$$

The mean number of H atoms exchanged is $4(1/4) = 1$

When these probability values are expressed as a ratio:

$$(CH_4) \approx 1$$

$$(CH_3D) \approx 1.25$$

$$(CH_2D_2) \approx 0.61$$

$$(CHD_3) \approx 0.15$$

$$(CD_4) \approx 0.013$$

The equilibrium distribution of the deuterated species from ref(12) are:

$$(CH_4) \approx 1$$

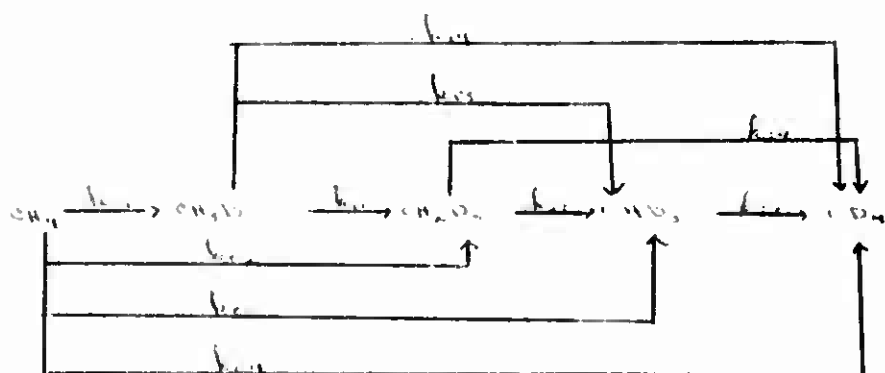
$$(CH_3D) \approx 1.25$$

$$(CH_2D_2) \approx 0.61$$

$$(CHD_3) \approx 0.15$$

$$(CD_4) \approx 0.013$$

Thus far it has been assumed that only one H-D exchange can occur when a specie contacts the surface. If more than one H-D exchange can occur on contact with the surface, the following diagram represents the ways in which deuterated species can be formed:



When first order reaction kinetics are assumed, the rate expressions are:

$$\begin{aligned} \frac{d(C_{CH_4})}{dt} &= -(k_{11} + k_{12} + k_{13} + k_{14}) (C_{CH_4}) \\ \frac{d(C_{CH_3OH})}{dt} &= k_{11} (C_{CH_4}) - (k_{12} + k_{13} + k_{14}) (C_{CH_3OH}) \\ \frac{d(C_{CH_3O_2H})}{dt} &= k_{12} (C_{CH_3OH}) + k_{15} (C_{CH_4}) - (k_{16} + k_{17}) (C_{CH_3O_2H}) \\ \frac{d(C_{H_2O})}{dt} &= k_{16} (C_{CH_3O_2H}) + k_{18} (C_{CH_3OH}) + k_{19} (C_{CH_4}) - k_{20} (C_{H_2O}) \\ \frac{d(C_{CO_2})}{dt} &= k_{14} (C_{CH_3O_2H}) + k_{21} (C_{CH_3OH}) + k_{22} (C_{CH_4}) + k_{23} (C_{CH_3O_2H}) \end{aligned}$$

The solutions to these expressions using the techniques described in Appendix A are:

$$\begin{aligned} (C_{CH_4}) &= (C_{CH_4})_0 e^{-\lambda t} \\ (C_{CH_3OH}) &= (C_{CH_4})_0 \left\{ \frac{k_{11}}{\lambda} \left(e^{-\lambda t} - e^{-k_{12} t} \right) \right\} \\ (C_{CH_3O_2H}) &= (C_{CH_4})_0 \left\{ \frac{k_{12}}{\lambda} \left(e^{-\lambda t} - e^{-k_{16} t} \right) + k_{15} k_{16} \right. \\ &\quad \left. \left[\frac{e^{-\lambda t}}{\lambda(k_{16} - \lambda)} + \frac{e^{-k_{16} t}}{\lambda(k_{12} - k_{16})} + \frac{e^{-k_{17} t}}{\lambda(k_{17} - k_{16})} \right] \right\} \\ (C_{H_2O}) &= (C_{CH_4})_0 \left\{ \frac{k_{16}}{\lambda} \left(e^{-\lambda t} - e^{-k_{16} t} \right) \right. \\ &\quad + k_{18} k_{16} \left[\frac{e^{-\lambda t}}{\lambda(k_{16} - \lambda)} + \frac{e^{-k_{16} t}}{\lambda(k_{12} - k_{16})} + \frac{e^{-k_{17} t}}{\lambda(k_{17} - k_{16})} \right] \\ &\quad + k_{19} k_{16} \left[\frac{e^{-\lambda t}}{\lambda(k_{16} - \lambda)} + \frac{e^{-k_{16} t}}{\lambda(k_{12} - k_{16})} + \frac{e^{-k_{17} t}}{\lambda(k_{17} - k_{16})} \right] \\ &\quad \left. - k_{20} k_{16} \left[\frac{e^{-\lambda t}}{\lambda(k_{16} - \lambda)} + \frac{e^{-k_{16} t}}{\lambda(k_{12} - k_{16})} + \frac{e^{-k_{17} t}}{\lambda(k_{17} - k_{16})} \right] \right\} \end{aligned}$$

the parameters can be postulated. If the experimental data can not be explained under any conditions, then the model created is not applicable.

The generalized linear differential equation

$$\frac{dx_i}{dt} = a_i + \sum_{j=1}^N k_{ij} x_j \quad i = 1, 2, \dots, N$$

can be rewritten in matrix notation

$$\frac{d}{dt} \begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_N \end{bmatrix} = \begin{bmatrix} k_{11} & k_{12} & \dots & k_{1N} \\ k_{21} & k_{22} & \dots & k_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ k_{N1} & k_{N2} & \dots & k_{NN} \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_N \end{bmatrix} + \begin{bmatrix} a_1 \\ a_2 \\ \vdots \\ a_N \end{bmatrix}$$

$$\text{or } \dot{X} = KX$$

The solution of this matrix equation is $X = e^{Kt} X_0$, where

$$\begin{bmatrix} x_1(t) \\ x_2(t) \\ \vdots \\ x_N(t) \end{bmatrix} = \begin{bmatrix} e^{k_{11}t} & e^{k_{12}t} & \dots & e^{k_{1N}t} \\ e^{k_{21}t} & e^{k_{22}t} & \dots & e^{k_{2N}t} \\ \vdots & \vdots & \ddots & \vdots \\ e^{k_{N1}t} & e^{k_{N2}t} & \dots & e^{k_{NN}t} \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_N \end{bmatrix}$$

where the vector X_0 is the value of $x(t)$ as $t \rightarrow 0$.

Equation (15) shows the solution of the matrix e^{Kt} is

$$e^{Kt} = \sum_{j=1}^N \frac{\prod_{i=1, i \neq j}^N (\lambda_i I - K)}{\prod_{i=1, i \neq j}^N (\lambda_i - \lambda_j)} e^{\lambda_j t}$$

where the λ_i ($i = 1, 2, \dots, N$) are the N distinct eigenvalue roots of the determinant K .

Using this method of solution, Equation (16) shows the solution for the reaction

$$c_1 A_{11} + c_2 A_{12} + \dots + c_n A_{1n}$$

The rate differential equations are:

$$\begin{aligned}\frac{dC_1}{dt} &= -k_{11}C_1 \\ \frac{dC_2}{dt} &= k_{12}C_1 - k_{22}C_2 \\ \frac{dC_3}{dt} &= k_{23}C_2\end{aligned}$$

In matrix notation, $\dot{C} = KC$

the solution being $C(t) = e^{Kt}C_0$

$$C(t) = e^{Kt} \begin{bmatrix} C_{10} \\ C_{20} \\ C_{30} \end{bmatrix}$$

The characteristic roots of K are given by the roots of the determinant

$$|\lambda I - K| = 0$$

$$\begin{vmatrix} \lambda + k_{11} & 0 & 0 \\ -k_{12} & \lambda + k_{22} & 0 \\ 0 & -k_{23} & \lambda \end{vmatrix} = 0$$

The characteristic roots are $\lambda_1 = -k_{11}$, $\lambda_2 = -k_{22}$, $\lambda_3 = -k_{23}$

The solution of the system is

$$C(t) = \sum_{i=1}^n \frac{1}{\prod_{j \neq i} (\lambda_i - \lambda_j)} \left(\frac{C_{10}}{\lambda_i + k_{11}} + \frac{C_{20}}{\lambda_i + k_{22}} + \frac{C_{30}}{\lambda_i + k_{23}} \right) e^{\lambda_i t}$$

evaluating the matrix products for $\lambda_1, \lambda_2, \lambda_3$

$$e^{Kt} = \frac{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)} e^{\lambda_1 t} + \frac{(\lambda_3 - \lambda_1)(\lambda_2 - \lambda_1)}{(\lambda_1 - \lambda_2)(\lambda_3 - \lambda_2)} e^{\lambda_2 t} + \frac{(\lambda_1 - \lambda_2)(\lambda_3 - \lambda_1)}{(\lambda_1 - \lambda_2)(\lambda_3 - \lambda_2)} e^{\lambda_3 t}$$

When these products are formed and addition made by matrix addition.

$$e^{Kt} = \begin{bmatrix} e^{\lambda_1 t} & 0 & 0 \\ \frac{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)} e^{\lambda_1 t} & e^{\lambda_2 t} & 0 \\ \frac{(\lambda_3 - \lambda_1)(\lambda_2 - \lambda_1)}{(\lambda_1 - \lambda_2)(\lambda_3 - \lambda_2)} e^{\lambda_2 t} & \frac{(\lambda_1 - \lambda_2)(\lambda_3 - \lambda_1)}{(\lambda_1 - \lambda_2)(\lambda_3 - \lambda_2)} e^{\lambda_3 t} & 1 \end{bmatrix}$$

Substituting e^{Kt} into $C(t) = e^{Kt} C_0$

$$\begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix} = \begin{bmatrix} e^{\lambda_1 t} & 0 & 0 \\ \frac{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)} e^{\lambda_1 t} & e^{\lambda_2 t} & 0 \\ \frac{(\lambda_3 - \lambda_1)(\lambda_2 - \lambda_1)}{(\lambda_1 - \lambda_2)(\lambda_3 - \lambda_2)} e^{\lambda_2 t} & \frac{(\lambda_1 - \lambda_2)(\lambda_3 - \lambda_1)}{(\lambda_1 - \lambda_2)(\lambda_3 - \lambda_2)} e^{\lambda_3 t} & 1 \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix}$$

In instances where the initial concentrations are zero except for (C_1) , where at $t = 0, C_1 = C_0$, only the first column of the matrix e^{Kt}

need be formed, which can obviously reduce the work required in multiplying matrices.

The above technique can be used for the rate equations for single site reactions involving two or three sites. In the latter case, the rate constants for the reactions are $k_1, k_2, k_3, k_4, k_5, k_6$, etc., and the initial concentrations are $C_1, C_2, C_3, C_4, C_5, C_6$, etc.

D. Conclusions

Exact expressions have been derived for H-D exchange of methane on a surface of adsorbed deuterium. While the expressions are awkward to handle, valid approximations are available which will ease calculations.

From the symmetry of the expressions for the multiple site exchange, it appears that the expressions for other molecules can be deduced with a minimum of calculations.

There are several advantages to this method of solving kinetic expressions over calculus methods. In particular the matrix operations can be conveniently handled by a digital computer, not only to derive the concentration expressions but also to substitute experimental values into the rate expressions. Also in the matrix form, perturbation matrices can be included to apply any necessary corrections for temperature, flow rates, etc., without disturbing the original rate constant expressions.

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13 ABSTRACT			
<p>A characterization of electrolyte conductivity in aqueous solutions involved two specific tests. The first involved the measurement of the conductivity of organic inorganic liquids which had been subjected to the energy loss rate. The conductivity of organic liquids was 1.5 mhos/cm, 1.7, in propylene carbonate, 1.7, in dimethyl sulfoxide, 3.7, and in tri-n-butylamine, 1.7. The conductivity of the organic liquids was measured at 25°C. low temperature with literature values for the conductivity of organic liquids. The conductivity of the organic liquids was measured due to the use of a conductivity cell with a 1.0 cm diameter electrode. The conductivity of the organic liquids was measured at 25°C. low temperature with literature values for the conductivity of organic liquids. The conductivity of the organic liquids was measured due to the use of a conductivity cell with a 1.0 cm diameter electrode. The conductivity of the organic liquids was measured at 25°C. low temperature with literature values for the conductivity of organic liquids. The conductivity of the organic liquids was measured due to the use of a conductivity cell with a 1.0 cm diameter electrode.</p>			

DISCUSSION

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